

# Impact of Stepwise Desulfation on the Performance of a Ba-Based Commercial Lean NO<sub>x</sub> Trap Catalyst

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## Introduction

The Lean NO<sub>x</sub> Trap (LNT) is being implemented in lean-burn vehicles for NO<sub>x</sub> aftertreatment. However, for its broader deployment, significant technical improvement is necessary especially with respect to sulfur poisoning. The LNT NO<sub>x</sub> storage components (Ba, K) have greater affinity for exhaust sulfur, and thus progressively lose their NO<sub>x</sub> storage capacity over time. As a result, high-temperature reductant-rich exhaust conditions are created periodically to “desulfate” the catalyst and regain its performance. The challenge is to develop more S-resistant LNTs and more effective strategies to desulfate while minimizing the fuel penalty and thermal aging arising from these high temperature excursions. Meeting this challenge will require deeper insights into how sulfation/desulfation affects LNT catalysis under relevant conditions. In addition to NO<sub>x</sub> storage materials, practical LNTs contain various other functions such as precious metals (Pt, Pd, Rh), supports (Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, TiO<sub>2</sub>), and oxygen storage capacity (CeO<sub>2</sub>-ZrO<sub>2</sub>). These components, through complex spatiotemporal interplay, determine LNT performance. Previously, we found that several LNT functions can be affected by S and proposed a conceptual model correlating spatiotemporal reaction distribution and global performance of a commercial LNT [1]. In this work, we addressed the desulfation aspect of the same LNT to further clarify the nature, distribution and roles of different S species by assessing the influence of stepwise desulfation on LNT performance.

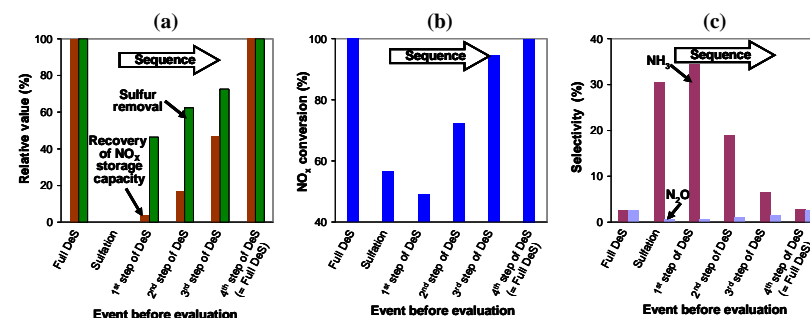
## Materials and Methods

A commercial Umicore LNT was evaluated on a bench reactor; details of the catalyst and reactor can be found in [1]. From ICP, XRD, EPMA, and TEM analyses, the catalyst was found to contain mainly two distinct domains: i) “active LNT” comprising Pt, Pd, Rh, Ba supported on CeO<sub>2</sub>-ZrO<sub>2</sub>; and ii) MgAl<sub>2</sub>O<sub>4</sub>. A fresh sample was degreened via hydrothermal treatment and six sulfation/desulfation steps to obtain reproducible performance. Total NO<sub>x</sub> storage capacity (lean portion of 15/10-min lean/rich long cycling), NO<sub>x</sub> conversion and NH<sub>3</sub>/N<sub>2</sub>O selectivity (both from 60/5-s lean/rich short cycling) were determined at 400 °C before and after sulfation (3.4 g/L) and after each of four consecutive desulfation steps (temperature ramp at 5 °C/min from 400 °C to maximum temperature T<sub>max</sub>: 492, 525, 564, 690 °C). The lean phase contained 300 ppm NO, 10% O<sub>2</sub>, 5% H<sub>2</sub>O, 5% CO<sub>2</sub> and N<sub>2</sub> balance, while the rich phase contained H<sub>2</sub> (0.4% for long and 3.4% for short cycling), 5% H<sub>2</sub>O, 5% CO<sub>2</sub> and N<sub>2</sub> balance. The gas composition was determined by FT-IR, SO<sub>2</sub>/H<sub>2</sub>S analyzers, and SpaciMS. The sample was characterized with various techniques including DRIFTS.

## Results and Discussion

Sulfation decreased NO<sub>x</sub> storage and conversion, but increased NH<sub>3</sub> selectivity (Fig. 1). This increased NH<sub>3</sub> was previously explained by reduced oxidation of NH<sub>3</sub> by downstream oxygen storage components based on spatially resolved gas analyses using

SpaciMS [1]. Briefly, the plug-like poisoning of Ba sites resulted in an axial displacement of the NH<sub>3</sub>-forming NO<sub>x</sub>-storage-reduction zone and concomitant shortening of the downstream oxygen-storage-only zone. The consecutive desulfation steps progressively reversed these trends (Fig. 1). However, the relationship between incremental S removal and resultant performance recovery was not linear. For example, the 1<sup>st</sup> desulfation step (T<sub>max</sub>=492 °C) produced insignificant performance recovery despite 46% S removal. The S removed in this 1<sup>st</sup> step was primarily associated with CeO<sub>2</sub>-ZrO<sub>2</sub> and other supports in the catalyst front. The implication is that this “containment” of 46% S in the catalyst front minimized S impact on downstream NO<sub>x</sub> storage sites. The slight degradation of short cycling performance (Figs. 1b and 1c) is likely due to partial readsorption of the upstream-released S onto downstream NO<sub>x</sub> storage sites. The 2<sup>nd</sup> and 3<sup>rd</sup> steps together removed only 26% S, but resulted in major recovery of NO<sub>x</sub> conversion and NH<sub>3</sub>/N<sub>2</sub>O selectivity. A remarkable impact of the 4<sup>th</sup> step (T<sub>max</sub>=690 °C; removal of remaining 28% S) is the recovery of over 50% of the total NO<sub>x</sub> storage capacity with minor impact on NO<sub>x</sub> conversion and NH<sub>3</sub>/N<sub>2</sub>O selectivity.



**Figure 1.** Performance of a Ba-based commercial LNT as a function of desulfation extent: (a) total sulfur removal and recovery of total NO<sub>x</sub> storage capacity, (b) cycle-averaged NO<sub>x</sub> conversion, and (c) cycle-averaged NH<sub>3</sub> and N<sub>2</sub>O selectivities.

Based on characterization (TPR, SpaciMS etc.), we attributed S from the 2<sup>nd</sup> through 4<sup>th</sup> steps to Ba sulfates. It follows that only a small portion of Ba was necessary to achieve full conversion under short cycling conditions. N<sub>2</sub>O selectivity remained low throughout the experiments. Interestingly, N<sub>2</sub>O and NH<sub>3</sub> followed opposite trends suggesting that N<sub>2</sub>O might be a minor product of oxidizing upstream-formed NH<sub>3</sub> by downstream oxygen species. In this presentation, we will discuss in detail the nature and distribution of different sulfur species and how their mobility under desulfation conditions affects local and global LNT performance.

## Significance

This work provides fundamental insights on how desulfation at different temperatures affects the distribution of sulfur species and as a result the global performance of a commercial LNT. The findings will be useful to design, model and implement real LNTs.

## Reference

1. Choi, J.-S., Partridge, W.P., and Daw, C.S., *Appl. Catal. B* 77, 145 (2007).